Basis and Purpose Document on Specifications For Hydrogen-Fueled Flares

Emission Standards Division

U.S. Environmental Protection Agency
Office of Air Radiation
Office of Air Quality Planning Standards
Research Triangle Park, North Carolina 27711

March 1998

DISCLAIMER

This Report has been reviewed by the Emission Standards Division of the Office of Air Quality Planning and Standards, EPA, and approved for publication. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use.

ENVIRONMENTAL PROTECTION AGENCY

Basis and Purpose
Document on Specifications for Hydrogen-Fueled Flare

1. The action for which this Basis and Purpose Document was written, amends the General Control Device Requirements (40 CFR part 60.18) which were issued as a final rule on January 21, 1986, and the Control Device Requirements (40 CFR part 63.11) which were issued as a final rule on March 16, 1994. The accompanying action adds specifications for hydrogen-fueled flares to the existing flare specifications for organic containing vent streams.

2. For additional information contact:

Mr. Robert Rosensteel
Organic Chemicals Group
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711
Telephone: (919) 541-5608

3. Paper copies of this document may be obtained from:

U.S. Environmental Protection Agency Library (MD-36)
Research Triangle Park, NC 27711
Telephone: (919) 541-2777

National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161
Telephone: (703) 487-4650

4. Electronic copies of this document may be obtained from the EPA Technology Transfer Network (TTN). The TTN is an electronic bulletin board system which provides information and technology exchange in various areas of emissions control. The TTN can be accessed through the TTN web site: www.epa.gov/ttn/oarpg/rules.html. For further information, contact the TTN HELP line at (919) 541-5384, from 1:00 p.m. to 5:00 p.m., Monday through Friday.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

The General Control Device Requirements of 40 CFR 60.18 were issued as a final rule on January 21, 1986 and are applicable to control devices complying with New Source Performance Standards (NSPS) promulgated by the Agency under Section 111 of the Clean Air Act (CAA), and National Emission Standards for Hazardous Air Pollutants (NESHAP) issued under the authority of Section 112 prior to the CAA Amendments of 1990. The Control Device Requirements of 40 CFR 63.11 were issued as a final rule on March 16, 1994 and are applicable to control devices used to comply with NESHAP issued under the authority of the CAA Amendments of 1990, for the control of hazardous air pollutants (HAP). Both of these existing control device requirements contain specifications defining required operating conditions of control devices. Specifically, 40 CFR 60.18(b) through (d), and 40 CFR 63.11(b) contain the operating conditions for flares (i.e., existing flare specifications). Flares operating in accordance with these specifications destroy volatile organic compounds (VOC) or volatile hazardous air pollutants (HAP) with a destruction efficiency of 98 percent or greater. These existing flare specifications were written for flares combusting organic emission streams.

E.I. DuPont de Nemours and Company (DuPont) representatives requested that the EPA either add specific limits for hydrogen-fueled flares to the existing flare specifications or approve their hydrogen-fueled flares as alternate means of emission limitation under 40 CFR 60.484, 40 CFR 61.12(d) and 40 CFR 63.6(g). DuPont subsequently sponsored a testing program to demonstrate that hydrogen-fueled flares in use at DuPont destroy emissions with 98 percent or greater efficiency. The test program demonstrated that these hydrogen-fueled flares achieved greater than 98 percent destruction efficiency. Further, the EPA judged the conditions of the test program to be universally applicable, with certain limitations. This document provides the background and rationale for the action to add specifications for hydrogen-fueled flares to the existing flare specifications.

This document is organized as follows. After this introduction, Section 2.0 provides background of the existing flare specifications and the studies used to establish them, along with a description of DuPont's hydrogen-fueled flare status. Section 3.0 summaries the DuPont program that was designed to demonstrate that their hydrogen-fueled flares were equivalent to flares meeting the existing flare specifications. Section 4.0 provides a summary of the hydrogen-fueled flare specifications that are being added to the existing flare specifications, and Section 5.0 contains the rationale for these recommended hydrogen-fueled flare specifications. Section 6.0 provides a summary of the anticipated impacts, and Section 7.0 summarizes this document. In this document, references are noted by their docket item number in Docket A-97-48. Appendix A to this document is the index for the relevant portions of Docket A-97-48.

2.0 BACKGROUND

2.1 Existing Flare Requirements

Flares are commonly used in industry to safely combust VOC and volatile HAP. Flares can accommodate fluctuations in VOC or volatile HAP concentrations, flow rate, heating value, and inerts content. Further, flares are appropriate for continuous and intermittent flow applications. Some organic emission streams can be flared without the need for supplemental fuel. However, the use of supplemental organic fuel such as natural gas to ensure the complete combustion of emissions is common.

The existing flare specifications contained in 40 CFR 60.18 and 40 CFR 63.11 are based upon experience with waste streams containing organic substances. These existing flare provisions require that the waste gas being flared have a minimum heat content, which is specific to the flare head design, and a maximum waste gas flow rate. The rules mandate that flares be designed for, and operated with, no visible emissions, except for periods not to exceed a total of five minutes during any two consecutive hours. In addition, the existing flare specifications require that the flare must be operated with a flame present at all times. The presence of a flare pilot flame is to be monitored to ensure that a flame is present at all times. The minimum net heating value of the gas being combusted and the maximum exit velocity of steam assisted, air assisted, and nonassisted flares, as specified in 40 CFR 60.18 and 40 CFR 63.11, are provided in Table 1.

TABLE 1. GENERAL CONTROL DEVICE REQUIREMENTS FOR FLARES CONTAINED IN 40 CFR 60.18. AND 40 CFR 63.11

Flare Type	Net Heating Value of Combusted Gas, H_T (megajoules per standard cubic meter)	Allowable Velocity, V (meters per second)
Air-Assisted	$11.2 \le H_T$	$V < V_{max}$[a]
Steam-Assisted	$11.2 \le H_T$	$V < 18.3$
Nonassisted	$7.45 \le H_T$	$V < 18.3$
Steam-Assisted or Nonassisted	$37.3 < H_T$	$18.3 \le V < 122$
Alternative for Steam-Assisted or Nonassisted	$11.2 \le H_T \le 37.3$	$V < V_{max}$[b] and, $V < 122$

[a]$V_{max} = 8.706+0.7084(H_T)$
[b]$\log_{10}(V_{max}) = (H_T + 28.8)/31.7$

As shown in Table 1, air-assisted flares must operate with an exit velocity less than the calculated maximum allowable velocity, V_{max}, which is calculated from an equation. Also, an equation is provided to calculate the maximum exit velocity for nonassisted and steam-assisted flares, as an alternative to the allowable velocities listed in the table. With steam-assisted and nonassisted flares, there are two options: (1) calculate the maximum allowable velocity from the equation, and verify that the exit velocity is below the calculated maximum allowable velocity, or (2) verify that the exit velocity is below the given V_{max} values for the heat content of the stream. Table 1 lists the allowable velocities for the possible heat contents.

The net heating value of the gas being combusted in a flare, which the owner/operator is required to calculate for all flare types, is calculated using Equation 1.

Equation 1:

$$H_T = K \sum_{i=1}^{n} C_i H_i$$

where:

H_T = Net heating value of the sample, Mega Joules per standard cubic meter (MJ/scm); where the net enthalpy per mole of off-gas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C.

$$K = Constant = 1.740X10^{-7}\left(\frac{1}{ppmv}\right)\left(\frac{g\text{-}mole}{scm}\right)\left(\frac{MJ}{kcal}\right)$$

where: ppmv = parts per million by volume, and
kcal = kilo calories

C_i = Concentration of sample component i in ppmv on a wet basis, as measured for organics by Method 18, 40 CFR part 60, appendix A, and measured for hydrogen and carbon monoxide by American Society for Testing and Materials (ASTM) Method D1946-77 (incorporated by reference as specified in 40 CFR 63.14 and 40 CFR 60.17).

H_i = Net heat of combustion of sample component i, kcal/g-mole at 25°C and 760 mm Hg. The heats of combustion may be determined using ASTM Method D2382-76 (incorporated by reference as specified in 40 CFR 63.14 and 40 CFR 60.17) if published values are not available or cannot be calculated.

n = Number of sample components.

2.2 Organically-Fueled Flare Studies Used to Establish the Existing Specifications for 40 CFR 60.18 and 40 CFR 63.11

The EPA determined the destruction efficiency of flares combusting volatile organic emissions in the early 1980's and developed the existing flare specifications as a result of this work. The testing was conducted with a nominal 8-inch diameter flare head furnished by a vendor (Docket No. A-97-48, Item No. I-II-12) and pilot-scale flares (Docket No. A-97-48, Item No. I-II-5).

In general, the experiments discussed showed that propane-in-nitrogen mixtures generate stable flames when the heat content of the mixture is above 200 Btu/scf. These experiments also showed that the combustion and destruction efficiencies of flares with waste streams containing organic substances are high (at least 98 percent) as long as the flame produced by the flare head at the given operating conditions was stable, based upon gas heat content and velocity.

2.3 DuPont’s Hydrogen-Fueled Flare Status

DuPont owns and operates six flares which are used to combust waste gases containing hydrogen (from 13 to 22 volume percent), inert gases (nitrogen, argon, carbon dioxide, and steam), oxygen (in some streams), and various combinations of the hazardous air pollutants (HAP) in the 115 ppm to 5 percent mole fraction (by volume) concentration range.

These six DuPont flares are nonassisted (pipe) flares, and each flare is similar in respect to the amount of hydrogen in the gas stream. The hydrogen and other flammable gas concentrations are such that gas heating values are in the range of 59 to 120 Btu/scf. Typical exit velocities for DuPont's hydrogen-fueled flares are on the order of 100 ft/s. All six of DuPont's hydrogen-fueled flares are equipped with continuous pilots to ensure flame stability.

As stated in the previous section, the existing flare specifications are based upon existing data which show that combustion efficiencies greater than 98 percent are achieved when specific heat content and velocity requirements are met. These data also show that combustion efficiency is related to flame stability. A flame is considered stable when the heating value is high enough to sustain a flame that is void of separations between the flare tip and any part of the flame.

Because the concentrations of the combustible gases are low, and because the heating value of hydrogen per unit of volume is low, the DuPont waste streams have low volumetric heat contents compared with streams containing volatile organics. Therefore, DuPont's flares do not meet the existing flare specifications of 40 CFR 60.18 and 40 CFR 63.11. As discussed earlier, these standards, developed primarily for flares with waste streams containing organic substances, set minimum heat content limits and maximum velocity specifications at which the flare can operate. To bring DuPont's hydrogen-fueled flares into compliance with the existing flare specifications would require the heat content of the waste stream be augmented with natural gas. DuPont estimates that the cost of the natural gas would be approximately $2.8 million per year in order for their six hydrogen-fueled flares to meet the existing flare specifications.

In March of 1997, DuPont requested that the EPA either add specific limits for hydrogen-fueled flares to the existing flare specifications or approve their hydrogen-fueled flares as alternate means of emission limitation (Docket No. A-97-48, Item No. II-D-2). DuPont subsequently sponsored a testing program to demonstrate that hydrogen-fueled flares in use at DuPont destroy emissions with greater than 98 percent efficiency. Following is a summary of DuPont's program.

3.0 SUMMARY OF DUPONT PROGRAM

To support petitions to the EPA for approval of hydrogen-fueled flares as equivalent in performance to the requirements of 40 CFR 60.18 and 40 CFR 63.11, DuPont initiated a two-phase program. The first phase was to gather background information on hydrogen-fueled flare studies, and the second phase was the testing program.

3.1 Background on Hydrogen-Fueled Flare Studies

The objective of the first phase of DuPont's study was to assemble available information on the flaring of hydrogen and hydrocarbon gas mixtures to support DuPont's equivalency claim for hydrogen-fueled flares. The conclusions of DuPont’s Phase I study (Docket A-97-48, Item II-I-2) were reported as follows.

- A large body of data exists on the combustion efficiency of flares incinerating volatile organic waste gas mixtures. These data show that the combustion efficiency is related to flame stability.

- Federal regulations are based upon existing data on the flaring of waste streams containing volatile organic substances, which demonstrate that combustion efficiencies greater than 98 percent are achieved when specific heat content and velocity requirements are met.

- Available information on flaring of hydrogen-based waste gas mixtures indicates that hydrogen gas mixtures can be burned over a significantly wider range of velocities and heat content conditions than organic gas mixtures.

- The results of small scale flare and diffusion flame experiments can be used to develop stability limits for flaring of hydrogen-inert gas mixtures. However, there is a wide range of uncertainty in the stability limits of lean hydrogen-inert mixtures.

- DuPont's hydrogen-fueled flares appear to be operating at or within the stability limits established from small scale studies. However, unless it can be shown that DuPont's flares exceed the stability limits for lean hydrogen-inert gas mixtures, it is not believed that this information is sufficient to successfully petition the U.S. EPA for an exemption.

- This study was not able to locate any information relating the stability of hydrogen flames to their organic destruction efficiency. This is expected to be significant since a central argument in establishing the equivalency of hydrogen flares is that high combustion efficiency is concomitant with flame stability.

Further, the study concluded that it was not expected that the previous hydrogen flare studies could be used to petition for a variance for DuPont's flares. Therefore, the study recommended that the second phase of the program be implemented.

3.2 Testing Program

The second phase of DuPont's program was composed of a series of tests intended to demonstrate that the hydrogen-fueled flares at their facilities were achieving a volatile HAP and VOC destruction efficiency equal to or greater than that of flares meeting the existing flare specifications.

Testing Plan

The test program was designed to experimentally establish the stability limits and destruction efficiency of DuPont’s flares under the range of chemical compositions and operating conditions at the three DuPont facilities with the six hydrogen-fueled flares. The testing plan was made up of stability and destruction efficiency tests using a nominal 3-inch diameter flare under conditions otherwise representative of the DuPont flares. The nominal 3-inch diameter flare was chosen to provide a link with the previous flare combustion efforts (Docket A-97-48, Item Nos. II-I-3, 4, and 5), because that was the size of flare used for those studies as well. The specific goals of the test plan were (1) to quantify the stability envelope (minimum gas hydrogen content versus exit velocity for flame stability) for hydrogen/waste gas mixtures having hydrogen concentrations and velocities in the range of DuPont's flares, and (2) to determine the destruction efficiencies of a surrogate organic compound added to the flare gas, at selected combinations of gas composition and velocity that are known to produce stable flames.

<u>Test Results</u>

As noted above, the tests were designed to determine the flame stability envelope and the destruction efficiency that a stable flame at a set velocity is able to achieve. The experiments were done by establishing a stable flame at the desired velocity, then slowly decreasing the hydrogen flowrate and recording the velocity and hydrogen content at flame lift off and again at blow out. Lift off was defined as the time when a portion of the flame was permanently separated from the flare tip. Blow out was defined as complete absence of the flame.

The measurements of the hydrogen volume percent at lift off and blow out for the piloted and unpiloted nominal 3-inch (2.9 inch inner diameter) pipe flare are shown in Figure 1 as a function of velocity. Because the hydrogen content at lift off was essentially the same for flares with and without a pilot burner, a single line was fit to the data sets of lift off measurements for piloted and unpiloted flares; this is represented by the upper curve in Figure 1 and by Equation 2. The data point in the far upper right corner of the figure is an unexplained outlier that is inconsistent with all other data points and was excluded from the linear regression analysis of the lift off data set. The middle and lower curves in Figure 1 are the blow-out curves without and with a pilot, respectively.

Equation 2:

$$X_{H_2,\ lift\ off}(\%) = 0.078u(ft/s) + 6.0$$

$$16.3 \le u \le 122 \text{ ft/s, with and without a pilot}$$

where:

$X_{H2,\ lift\ off}$	=	The hydrogen content at lift off of piloted and unpiloted flames, percent.
u	=	The tip velocity, ft/s.

Destruction efficiencies were determined at eight different combinations of tip velocity, hydrogen content, ethylene content (ethylene was the surrogate for which the destruction efficiency was determined), the presence or absence of a pilot, and high and low wind conditions. In all cases, the destruction efficiencies were greater than 98 percent, at a level of 95 percent confidence. Further, control efficiencies greater than 98 percent were found at hydrogen contents below the lift-off curve.

The data used in the development of the existing flare specifications showed that 98 percent destruction efficiency was achievable by maintaining the heating value of the flare gas a critical value above the minimum heating value required for flame stability. The critical value was found to lie in the range from approximately 1.1 to 1.3 times the minimum heating value for flame stability.

A similar analysis was conducted for DuPont's current study of hydrogen-fueled flares. The reference condition for stability that was used was the hydrogen content of the flare at lift off. The measured mean ethylene destruction efficiencies and destruction efficiencies at the 95 percent confidence level are shown as a function of the ratio of the actual hydrogen content of the flare gas to the hydrogen content at lift off at the same tip velocity in Figure 2. As observed in Figure 2, all of the destruction efficiency at conditions more stable than lift off (stability ratio greater than 1) are above 99 percent. The DuPont report concluded that extrapolation of the data to the left of Figure 2 (i.e., for hydrogen content ratios less than 1.0) suggests that the destruction efficiency would be assured for values of the stability ratio greater than about 0.95 to 0.97. The report recommended that a conservative criterion for assuring 98 percent destruction in hydrogen flares is that the stability ratio, or ratio of the hydrogen content to that at lift off at the same tip velocity, be equal or greater than 1.0.

The choice of the hydrogen content at lift off as the critical condition places the ratio of the critical to the minimum value at blow out with pilot at the values shown in Table 2, as a function of tip velocity. As shown in Table 2, the excess hydrogen content for minimum flame stability is seen to increase from a low of 15 to 17 percent at the higher velocities tested, to around 30 percent at the lower velocities tested. These data relate the ratio of hydrogen content to the tip velocity and indirectly relate the tip velocity to the destruction efficiency in the following manner. As discussed previously, the hydrogen ratio is also directly proportional to the destruction efficiency (that is, as the ratio of hydrogen in the stream versus hydrogen at lift off increases, the destruction efficiency of the flame increases). Therefore, it can be concluded that the tip velocity and destruction efficiency are inversely proportional.

Following are the general conclusions and recommendations from the testing program.

- The results of the study generally agreed with the results of earlier studies on the stability and performance of hydrogen-fueled flares.

- The heat input to the flare through the pilot was found to have a significant effect on blow out at high values of the ratio of pilot to flare heat input.

- The hydrogen content at lift off was not strongly influenced by pilot type or heat input.

- The hydrogen content at lift off was the same for piloted and unpiloted flares.

- Blow out occurred at hydrogen contents approximately 1 mole percent less than lift off in the absence of a pilot, and 3 mole percent lower in the presence of a pilot.

- The destruction efficiency was greater than 98 percent, at a 95 percent confidence level, under all conditions investigated.

- Destruction efficiency increased slightly on increasing the ethylene content of the flare gas, indicating that the addition of organics at percent levels does not contribute to the deterioration of hydrogen-fueled flare performance.

- Destruction efficiencies greater than 98 percent were achieved at hydrogen contents as low as 0.955 times the hydrogen content at lift off. Destruction efficiencies greater than 99 percent (95 percent confidence level) were achieved at a ratio of hydrogen content to hydrogen content at lift off greater than 1.0.

- The combination of velocity and hydrogen volume fraction at lift off were recommended as the conservative criteria for greater than 98 percent destruction efficiency.

- Not all of DuPont's hydrogen-fueled flares meet the conservative conditions recommended, at the time of this testing.

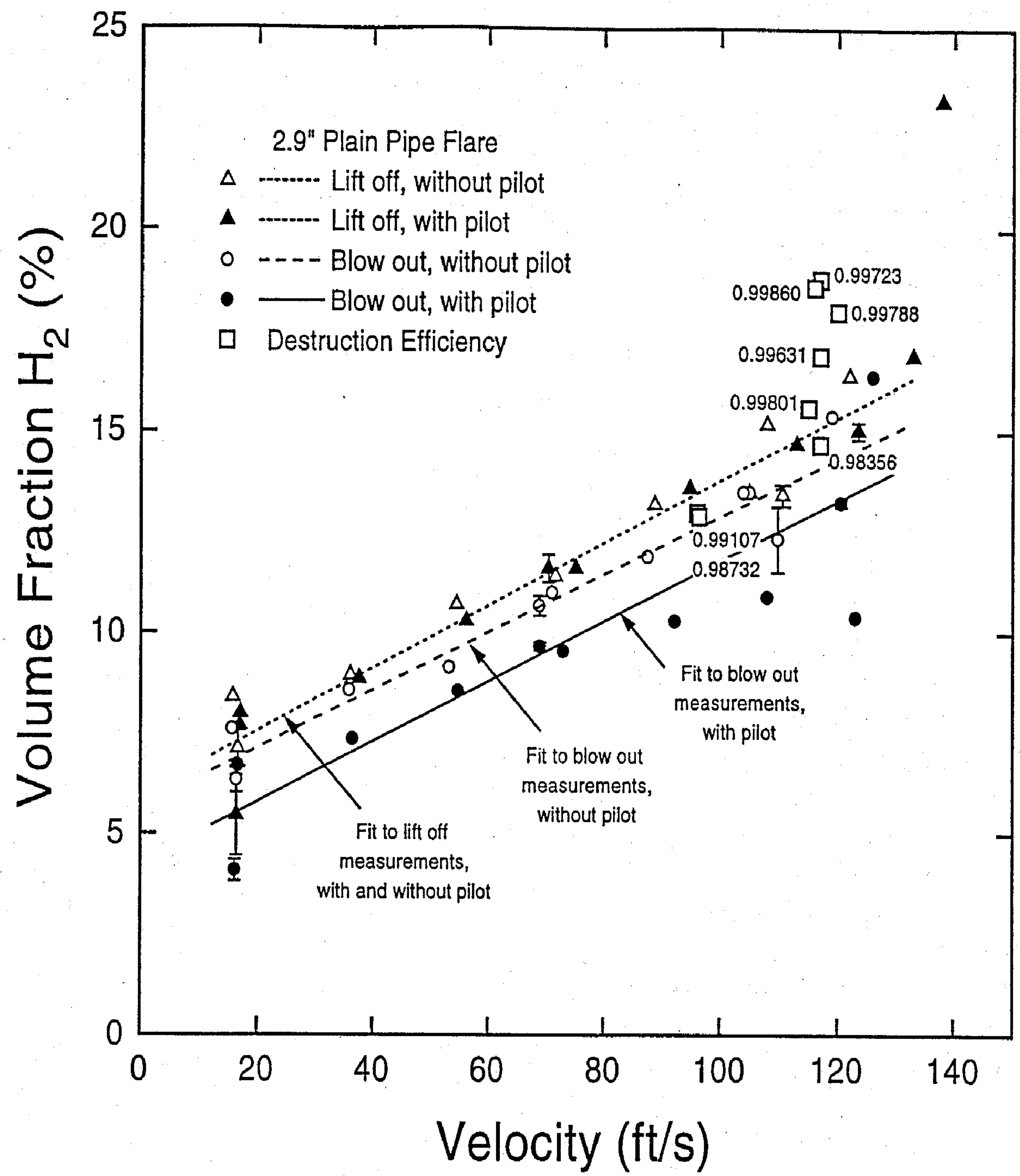

Figure 1. Hydrogen Volume Fractions at Lift-Off and Blow-Out Of A 2.9 inch plain pipe flare (Docket A-97-48, Item No. II-I-1)

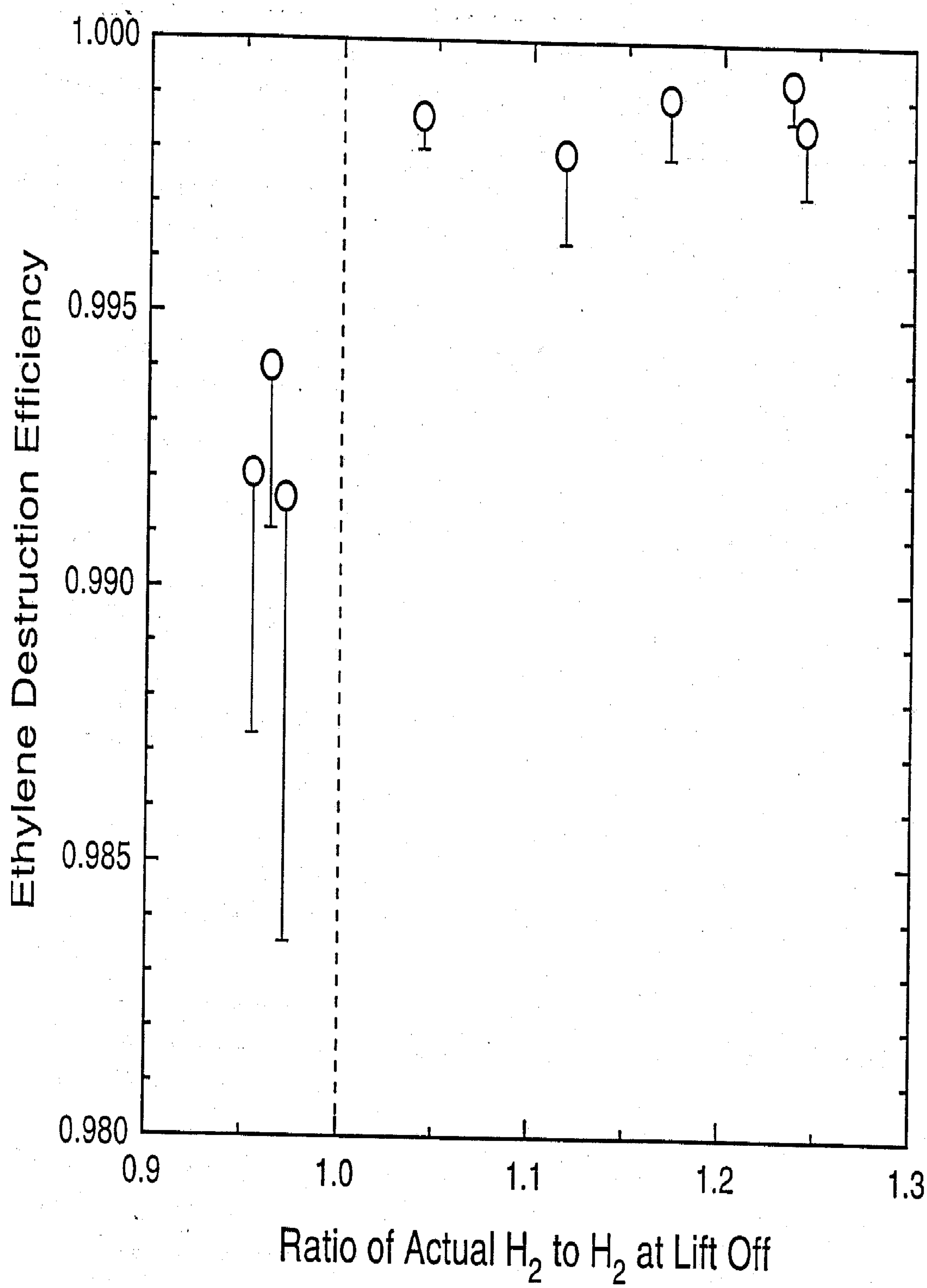

Figure 2. Relationship of Ethylene Destruction Efficiencies to the Ratio of Actual Hydrogen Content to the Hydrogen Content at Lift-Off (Docket A-97-48, Item No. II-I-1)

TABLE 2. DEPENDENCE ON TIP VELOCITY OF THE RATIO OF THE PROPOSED CRITICAL HYDROGEN VOLUME FRACTION TO THE HYDROGEN VOLUME FRACTION AT BLOW OUT WITH PILOT

Tip Velocity (ft/s)	Ratio of H_2 Content at Lift Off to the H_2 Content at Blow Out with Pilot
17	1.31
20	1.30
40	1.25
60	1.21
80	1.19
100	1.17
120	1.15

4.0 SUMMARY OF THE RECOMMENDED SPECIFICATIONS

The recommended hydrogen-fueled flare specifications add requirements for nonassisted flares that combust 8.0 percent (by volume) or greater of hydrogen in the stream and have a 3-inch or greater diameter. The recommended hydrogen-fueled flare specifications present an equation that calculates the maximum allowable flare tip velocity for a given volume percent of hydrogen. This equation format is similar to the one used for air-assisted flares in the existing flare specifications. The specific equation for the maximum tip velocity for hydrogen-fueled flares is:

$$V_{max} = (X_{H2} - K_1)^* K_2$$

Where:

V_{max} = Maximum permitted velocity, m/sec.

K_1 = Constant, 6.0 volume-percent hydrogen.

K_2 = Constant, 3.9(m/sec)/volume-percent hydrogen.

X_{H2} = The volume-percent of hydrogen, on a wet basis, as calculated by using the American Society for Testing and Materials (ASTM) Method D1946-77.

5.0 RATIONALE FOR THE RECOMMENDED SPECIFICATIONS

5.1 The Need for Specifications for Hydrogen-Fueled Flares

As discussed below, hydrogen has a lower heat content than organics commonly combusted in flares meeting the existing flare specifications and cannot, therefore, be used to satisfy existing control requirements. However, since the combustion of hydrogen is different than the combustion of organics, and the test report demonstrates a destruction efficiency greater than 98 percent, the EPA believes that hydrogen-fueled flares meeting the recommended specifications will achieve a control efficiency of 98 percent or greater. This level of control is equivalent to the level of control achieved by flares meeting the existing specifications. In addition to achieving the same destruction efficiency of VOC or organic HAP, these recommended specifications have the added advantage of reducing the formation of secondary pollutants; since the combustion of supplemental fuel would not be required by hydrogen-fueled flares to meet the existing flare specifications.

<u>The Heat Content of Hydrogen</u>

The heat content of a substance is a measure of the amount of energy stored within the bonds between atoms in each molecule of the substance. Hydrogen is a simple molecule consisting of two hydrogen atoms held together by weak, hydrogen bonds, thus resulting in a low heat content. In comparison, organic chemicals are larger chains (or rings) of carbons with hydrogens and other atoms attached to them. These molecules are held together with a combination of ionic, covalent and hydrogen bonds, which contain substantially more energy (i.e., higher heat content) than the hydrogen bond in the hydrogen molecule.

<u>The Difference in Combustion Between Hydrogen and Organics</u>

The first phenomenon to explain the difference in combustion between hydrogen and organics is related to the thermodynamics of the combustion reaction. In order for the hydrogen atom to react in the combustion/oxidation reaction, the weak hydrogen bond between the two hydrogen atoms must first be broken. Because there is less energy holding the hydrogen atoms together, less energy (heat) is required to separate them. Once the hydrogen bonds are broken, the hydrogen atoms are free to react in the combustion reaction.

The second phenomenon explaining the difference in combustion between hydrogen and organics is due to hydrogen's upper and lower flammability limits. The flammability limits are the minimum (lower) and maximum (upper) percentages of the fuel in a fuel-air mixture that can propagate a self-sustaining flame. The lower and upper flammability limits of hydrogen are 4.0 and 74.2 percent, respectively, which represents the second widest range of lower and upper limits of substances typically combusted in flares (Docket No. A-97-48, Item No. II-I-2).

The third phenomenon explaining the difference in combustion between hydrogen and organics is the relative difference in diffusivity between hydrogen and organics in air. Diffusivity refers to how easily molecules of one substance mix with molecules of another. Further, the quicker the fuel and air in a flare mix, the quicker the combustion reaction occurs. The measure of how quickly a substance mixes with another substances is expressed in terms of the diffusivity coefficient. The larger the diffusivity coefficient, the quicker the mixing. The diffusivity coefficient for the mixture of hydrogen and air is an order of magnitude higher than those for the mixture of air and volatile HAP with readily available diffusivity coefficients.

Therefore, hydrogen is more diffuse in air compared to organics and more quickly enters the flammability range than organics.

5.2 Use of DuPont Test Results as the Basis for Hydrogen-Fueled Flare Specifications

In selecting the conditions under which the pilot flare testing was to be conducted and interpreting the results of the testing, a "conservative" decision was made for each choice. That is, the condition that would most likely assure that a full-scale flare would achieve at least as high and possibly higher destruction efficiency was chosen. This approach was applied to the selection of flare tip design, flare tip diameter, pilot burner heat input, and characteristics of the surrogate for HAP for destruction testing. It was also applied to the evaluation of stability testing and destruction efficiency results, as well as the selection of operating limits applying to hydrogen concentration and tip discharge velocity.

The Selection of the Flare Type

A nonassisted, plain-tip flare was used in the testing program because all of DuPont's flares are nonassisted. A nonassisted flare is a flare tip without any auxiliary provision for enhancing the mixing of air into its flame. The plain-tip means no tabs or other devices to redistribute flow were added to the rim of the flare. Because the presence of tabs improves the stability of the flare by channeling the flare's flow and improving mixing of fuel and air, it was concluded that the lack of tabs (i.e., plain tip) would result in the least stable test conditions.

The Comparison of the Selected Flare with the Existing Flare Specifications

A 3-inch flare was selected for the emission test since this was the same size flare used for the testing to establish the basis for the existing flare specifications in 40 CFR 60.18 and

40 CFR 63.11. Stability tests were conducted using propane to determine if the flare was operating properly and could meet the existing flare specifications. Test results demonstrated that this flare was stable when it was expected to be stable and not stable when it was not expected to be (i.e., as indicated by the existing flare specifications).

The Size of the Test Flare

Another reason for using the 3-inch flare for these tests is because a 3-inch flare is small, relative to the size of flares in industry (as a point of reference, the DuPont flares are 16 to 48 inches in diameter). Research indicates that smaller flares are less stable than larger flares (Docket No. A-97-48, Item No. II-I-1, Sec 4, page 6). Specifically, the physical parameter known as the velocity gradient can be used to predict when a flame will blow out by plotting the velocity gradient versus the volume-percent hydrogen. The larger the boundary velocity gradient, the more unstable the flame. Further, the velocity gradient is inversely proportional to the diameter of the pipe. Therefore, at a given velocity, the larger the pipe, the smaller the boundary velocity, and the more stable the flame. The EPA concludes that if a stable flame can be maintained with a smaller flare pipe, then a larger flare would be expected to be stable at lower hydrogen concentrations and higher velocities. Therefore, the EPA believes that 3-inch or larger flares that meet these specifications will have destruction efficiencies as high or higher than those obtained from the 3-inch pipe flares.

The Selection of the Size of the Pilot Burner

The amount of heat input from the pilots on DuPont's full-scale hydrogen-fueled flares are in the range from 0.05 to 0.6 percent of the total heat input to the flares. A venturi burner turned down to approximately one third of its 9,000 Btu/hr capacity was used for the tests described in this document, and the heat input was equal to 0.3 to 0.6 percent of the pilot flare's total heat input during the stability and destruction efficiency tests. Therefore, the heat input from the pilot during the tests was comparable to the heat input for the full-scale flares operated by DuPont.

The relatively small proportion of heat input from the venturi burner compared to the total heat input to the test flare would not be expected to have a significant effect on either the stability or destruction efficiency results, because this amount of heat is insignificant compared to the flare's total heat content. Also, the use of a pilot burner is consistent with EPA's flare specification which requires that the pilot flame be present at all times.

The Selection of Ethylene as the Surrogate for HAP to be Used in the Testing

For this study, a surrogate for HAP that was more difficult to destroy than the volatile HAP present in the large scale flare waste streams, and which could be measured at a concentration of 10 parts per billion by volume and higher was selected. In general, the difficulty of destruction for organics increases as the molecular weight decreases, but the limit of detection decreases as the molecular weight decreases.

In order to compare the relative difficulty to destroy various species, a linear multiple regression model was used that calculates a destruction temperature using parameters describing the molecular structure, autoignition temperature, and residence time as inputs to the model. The destruction temperatures obtained are theoretical temperatures for plug flow reactors to achieve specified destruction allowing a comparison to be made among various chemical species to estimate relative destructibility (Docket No. A-97-48, Item No. II-I-14). As a first step, the destruction temperatures were calculated for all the chemical species that were identified in DuPont's full-scale flare waste streams. The next step was to calculate destruction temperatures for the surrogates for HAP under consideration.

(The results from this analysis are presented in Tables 4-3 and Table 4-4 of Docket Item II-I-14).

In comparing the model's destruction temperature estimates for candidate surrogates for HAP present in DuPont's flare streams, the best choice as a surrogate was methane, but the detection limit for methane was too high to be accepted for the field study. The next choice was methanol, but not only is the detection limit high for methanol, it is a HAP and is a liquid at ambient temperatures, presenting handling difficulties. The next candidate considered was ethylene which was selected for the study. Ethylene has an equivalent or higher destruction temperature than all the organic HAP in the study, except methanol, and has an acceptable limit of detection. Therefore, the substance that was the most difficult to destroy but feasible to use was chosen for the study.

The Criteria for a Stable Flame

The hydrogen content reported when lift off was first observed was selected as the criterion for a stable flame, because it was easy and precise to identify. The EPA concluded that this was a conservative estimate for the stability limit because destruction efficiencies greater than 98 percent were noted even for hydrogen contents below the lift off level.

The EPA also concluded that lift off was a conservative criterion for a stable flame, based on a correlation between the stability ratio and the destruction efficiency observed in earlier flare testing conducted in the 1980's (Docket No. A-97-48, Item No. II-I-5). At that time the destruction efficiencies were demonstrated to be directly proportional to the ratio of the flare gas heating value to the minimum heating value for flame stability (i.e., stability ratio). Regardless of the substance being combusted, or the flare design, it was observed that the destruction efficiency plateaued to greater than 98 percent destruction when the stability ratio was above approximately 1.2. For this test program, the destruction efficiency versus the ratio of actual hydrogen to hydrogen at lift off (analogous with the stability ratio, and referred to as the hydrogen ratio) was plotted for this test program. The curve of the data was similar to those obtained from the flare test programs in the 1980's. Three data points demonstrated that at stability ratios below 1.0, with the lowest stability ratio of 0.955, destruction efficiencies greater than 98 percent were achieved. Since these hydrogen-fueled flare specifications require a stability ratio of 1.0 or greater, it is assumed that a 98 percent or greater destruction efficiency will be achieved.

<u>The Operating Parameters Used for Testing the Destruction Efficiency (i.e., Hydrogen Content and Flare Tip Velocity)</u>

The destruction efficiency of ethylene for the hydrogen-fueled flares was tested at high tip velocities (i.e., approximately 100 to 120 ft/sec) because this is the velocity range expected to produce lower destruction efficiencies. Therefore, if acceptable destruction efficiencies are observed at high tip velocities, then at least as high or even higher destruction efficiencies are expected at lower tip velocities.

The expectation to observe decreased destruction efficiency at high tip velocities is explained by two phenomena. The first phenomenon is due to the increased fuel flow. The increased volume of fuel flow entrains more air, and more eddies are formed at the boundary between the fuel and the air. These eddies tend to strip off some of the gases' flow, even before the flame is able to combust the substances, so uncombusted or incompletely combusted substances may be lost to the ambient air.

Another phenomenon explaining the expectation of decreased destruction efficiency at increased tip velocities results from comparisons of stability ratios at different tip velocities. For this test program the ratio of the hydrogen content at lift off to the hydrogen content at blow out with a pilot was used as an analogous ratio to the previously mentioned stability ratio. Further, the value of hydrogen at blow out was used as the minimum hydrogen content, since at essentially this level of hydrogen, the destruction efficiencies were above 98 percent for tip velocities of 100 and 120 ft/sec. The DuPont test program's data revealed a trend where the hydrogen ratios were lower at higher velocities compared to lower tip velocities, 1.15 to 1.17 versus 1.3, respectively. Since the test programs in the 1980's demonstrated that the destruction efficiency is directly proportional to the stability ratio, then it could be expected that the same or higher destruction efficiencies would be experienced at lower tip velocities where the hydrogen ratios are larger.

5.3 Selection of the Specifications for Hydrogen-Fueled Flares

The recommended specification for hydrogen-fueled flares is the maximum tip velocity for a given hydrogen content (determined according to the equation of the line fitting the data from the stability testing at lift off conditions as seen in Figure 1). The equation in the recommended specifications comes directly from the test report. This equation is Equation 2, with the units changed to metric.

There are safety requirements that must be carefully considered for all flare installations, and this is the case for the use of these hydrogen-fueled flare specifications. As an example, if the discharge velocity is too low under certain conditions, the flame could propagate back into the process with potentially catastrophic results. These recommended specifications only specify a maximum discharge velocity for the purpose of assuring efficient destruction of pollutants in waste streams and do not address any aspect of safe operation. The user of any EPA flare specifications should carefully consider all features of this application, not just the limitation on maximum discharge velocity, and implement all necessary measures to assure a safe operation. Safe operating conditions are always the responsibility of the owner/operator at each facility to assure that all applicable safety requirements are adhered to whether they are company, consensus and/or governmental requirements.

The EPA did not think that extrapolating the data outside the range of values tested to be prudent; therefore, the hydrogen-fueled flare specifications have been restricted to the confines of the conditions used for the test program. The following restrictions are included in the hydrogen-fueled flare specifications:

Nonassisted Flares

The recommended hydrogen-fueled flare specifications are applicable to nonassisted flares, because it was the only type of flare tested.

Continuous Flame

The existing flare specifications require the presence of a continuous flame where reliable ignition is obtained by continuous pilot burners designed for stability. To ensure that the pilot is continuously lit, a flame detection device is required. These recommended hydrogen-fueled flare specifications incorporate the same requirements for the same reason, to ensure flame stability.

Minimum Flare Diameter

The testing was conducted on 3-inch flares, therefore this is the minimum flare diameter for the recommended hydrogen-fueled flare specifications.

Minimum Hydrogen Content

The minimum hydrogen content in the gas streams tested was rounded to the nearest whole number, 8.0 volume percent, and set as the defining minimum hydrogen concentration cutoff for a hydrogen-fueled flare.

Maximum Tip Velocity

The maximum tip velocity was set at 37.2 m/sec (122 ft/s), because that was the highest tip velocity tested.

Flame Stabilizers

Flame stabilizers (often called flame holders) are allowed because stability and destruction efficiency testing was conducted without them, so if these tabs stabilize the flame even better mixing, and potentially greater destruction efficiencies can be achieved.

Minimum Flare Tip Velocity

A minimum flare tip velocity was not listed since evidence indicates that performance will not be diminished due to lower tip velocities (See the preceding discussion concerning safety responsibilities).

6.0 SUMMARY OF ENVIRONMENTAL, ENERGY, AND COST IMPACTS

The impacts discussed in this section are only for six DuPont flares that are required by current or pending EPA regulations to meet the existing flare specifications. The EPA does not have information, and cannot estimate impacts for other hydrogen-fueled flares in the United States. Therefore, the following estimates are limited to these six DuPont flares.

6.1 Primary Air Impacts

The recommended flare specifications will reduce emissions by the same amount (i.e., 98 percent or greater) as emissions would be reduced by using flares meeting the existing flare specifications.

6.2 Other Environmental Impacts

The Agency estimates that the recommended hydrogen-fueled flare specifications will reduce secondary emissions of pollutants since the combustion of supplemental organic fuel will no longer be required; therefore, there will be no emissions resulting from the combustion of a supplemental fuel. It is estimated that these recommended hydrogen-fueled flare specifications will reduce annual emissions from the six affected DuPont flares by 147 megagrams (161 tons per year) of criteria pollutants (i.e., 124 megagrams (136 tons per year) of carbon monoxide, and 22.7 megagrams (25 tons per year) of nitrogen oxides) and 39,900 megagrams (44,000 tons per year) of carbon dioxide.

In addition to these secondary emission reductions, there may also be State regulations that require owners/operators to follow the existing flare specifications, and by allowing the owners/operators to meet these recommended hydrogen-fueled flare specifications, there may be further reductions in secondary air emissions. Therefore, these impacts are a minimal estimate of the potential secondary air emission reductions.

6.3 Energy Impacts

These recommended hydrogen-fueled flare specifications are expected to decrease the amount of energy used by DuPont's six hydrogen-fueled flares since the flares will no longer be required to combust secondary fuel. The expected energy savings is estimated to be 7.75×10^{8} cubic feet of natural gas annually (7.75×10^{11} Btu/yr) .

6.4 Cost and Economic Impacts

Cost savings will be realized due to the recommended hydrogen-fueled flare specifications by not requiring the combustion of supplemental fuel (to comply with the original heat content requirements), and by not requiring the subsequent resizing of the existing flares that would result from a requirement to combust supplemental fuel in order to accommodate the additional flow of supplemental fuel. The cost of natural gas as supplemental fuel for the six affected flares is estimated to be $2.8 million per year. The capital investment to replace a smaller flare tip with a larger one is estimated to be approximately $667,000 per flare or $4 million for all six flares. The total annual savings achieved by allowing hydrogen-fueled flares that fulfill the recommended specifications are the sum of the annual fuel cost savings, and the annualization of the capital savings (calculated to be $280,000 per year). Therefore, total annual savings for the six affected DuPont flares are estimated to be $3.08 million per year. Since sources using these hydrogen-fueled flare specifications will experience savings, no adverse economic impacts will result from the recommended hydrogen-fueled flare specifications.

6.5 Summary of Impacts

This section discussed the cost savings, emission reduction of secondary pollutants, and energy savings from only the six DuPont flares subject to current or pending regulations. The recommended hydrogen-fueled flare specification have greater potential to reduce emissions and save money and fuel from hydrogen-fueled flares that the EPA is currently aware.

7.0 SUMMARY

The purpose of this report is to describe the events leading up to the development of alternative flare specifications for hydrogen fueled flares, and to illustrate how test data supplied by DuPont were used to develop the recommended specifications. The report opens with a description of the existing flare specifications followed by a summary of the studies used to establish the criteria for the hydrogen-fueled flare specifications. The basic objectives of these sections were to provide the parameters for the existing rules and to establish that the existing flare specifications are based on the theory that HAP destruction can be equated with flame stability.

This report provides the basis for the alternative flare specifications which the EPA is recommending based on a request made by DuPont. To support their petition, DuPont provided experimental data as well as an account from a previous studies. Additionally, this report provides a descriptive summary of the data provided from DuPont’s tests and an analysis of each parameter utilized in the testing. The EPA believes that the results of the DuPont hydrogen-fueled tests provide the appropriate data to support the hydrogen-fueled flare specifications.

In closing, this report provides a summary of the recommended hydrogen-fueled flare specifications and an explanation of the rationale used to establish these recommended specifications. The EPA believes that flares meeting the recommended hydrogen-fueled flare specifications being added will achieve a destruction efficiency of at least 98 percent, and will result in cost savings to those industries that flare waste gases containing a hydrogen content of at least 8.0 percent.

APPENDIX

DOCKET INDEX FOR SUBCATEGORY II-I OF DOCKET A-97-48